ARPA Order No. 306-62
Project Code No. 4730

SEMIANNUAL TECHNICAL SUMMARY REPORT

FOR

HYDROTHERMAL GROWTH OF CRYSTALS OF $LaAlO_3$

1 July 1965 to 31 December 1965
NONR-4616(00)

Submitted by:
Airtron, a division of Litton Industries
200 East Hanover Avenue
Morris Plains, New Jersey

OFFICE OF NAVAL RESEARCH
NONR-4616(00)
ADVANCED RESEARCH PROJECTS AGENCY
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This research is a part of Project DEFENDER, sponsored by Advanced Research Projects Agency, Department of Defense, and technically monitored by the Office of Naval Research, under Contract NONR-4616(00).

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I. PURPOSE

Our primary objective is to grow large single crystals of $LaAlO_3$ doped with chromium from a hydrothermal system, using seed crystals produced from a molten salt system. Factors influencing the growth of large single crystals such as regions of congruent solubility, crystal stability, and degree of solubility will be examined.

II. ABSTRACT

Large single crystals of pale yellow $LaAlO_3$ (undoped) measuring approximately 1/2" x 1/2" x 1/4" were successfully grown in a 250 ml crucible from a Bi_2O_3-B_2O_3 flux. The ratio of B_2O_3 to Bi_2O_3 was an important consideration in the composition of the melt; compositions consisting of about 19 m % B_2O_3 appeared to produce the best growth. Larger B_2O_3 ratios produced a glassy melt from which no crystals grew while pure Bi_2O_3 yielded numerous small crystals no larger than 1 mm^3.

Weight gains of up to 36% have been achieved in the hydrothermal system using flux grown seeds Hydrothermally reacted and sintered $LaAlO_3$ pellets have been tried as nutrient. Also a hot pressed mixture of the component oxides was tried. Neither approach was completely successful, but each method shows some merit. One large autoclave failed due to cracks in the seal area during the report period It has been rebored, fitted with a liner and water tested successfully.

Optical absorption and fluorescence measurements have been made on flux and hydrothermally grown samples of $LaAlO_3$:Cr and on undoped flux grown $LaAlO_3$. The hydrothermally grown samples appear green due to the presence of a transmission band at 5300A°.

III. STATUS

This report covers the six month period July 1, 1965 to December 31, 1965. During this period success has been achieved in the growth from molten salt systems of large single crystals up to 1/2" x 1/2" x 1/4" in a 250 ml crucible. These crystals are of a size and quality suitable for hydrothermal seeds.

We have also continued our study of hydrothermal growth conditions by investigating nutrient sources and making adjustments of fill conditions as required by nutrient changes. Currently underway are attempts to grow $LaAlO_3$ crystals below and above the 435°C transition temperature in regions determined by the phase study.

Table I indicates the goals set forth for the current contract and their status. The most serious delay during this period was caused by the extremely corrosive nature of Bi_2O_3 especially when crucibles had been previously used with lead salts. Several cans leaked their contents upon the pedestal and the furnace had to be rebuilt. New crucibles, which have a delivery time of 6 to 8 weeks, had to be ordered. New crucibles, that have never been used with lead salts, have a lifetime of three to four runs.

TABLE 1

STATUS

Item	Goal	Purpose	Current Status	Problems Encountered or Expected	Estimated Completion Date
1	Selection of solvent system from which large $LaAlO_3$ crystals can be grown	Large seed crystals	Complete	Corrosion of Pt by Bi_2O_3	11/65
2	Determine solubility of doped and undoped $LaAlO_3$ in Bi_2O_3	Large seed crystals	Not started	None	5/66
3	Optimize growth conditions for large high quality crystals	Large seed crystals	Not started	None	7/66
4	Determine effect of temperature, pressure and ΔT on hydrothermal $LaAlO_3$	Provide data for large crystal growth runs	In progress	None	6/66
5	Determine effect of seed orientation and quality on hydrothermal quality	Provide data for large crystal growth runs	Not started	None	7/66
6	Grow large $LaAlO_3$ crystals hydrothermally	Contract objective	Not started	None	8/66
7	Lifetime measurements on hydrothermally grown crystals	Contract objective	Not started	None	8/66
8	Final report	Contract requirement	Not started	None	9/66

IV. MOLTEN SALT CRYSTAL GROWTH

A. Experimental

While large $LaAlO_3$ crystals can be grown from PbF_2 solutions, temperatures approaching 1500°C must be attained. So severe was furnace and platinum crucible attack at these temperatures that a search for a new solvent system was started in spite of the success which had been achieved with PbF_2.

A summary of all molten salt runs made during this period is shown in Table II The following systems were investigated.

1) $PbO-B_2O_3$

This flux has been successfully used to grow large $PrAlO_3$ crystals. Runs 80 and 81 (see Table II) used 64.20 m% PbO and 20.60 m% B_2O_3 to dissolve 7.60 m% La_2O_3 and Al_2O_3 respectively.

Run No. 81 was heated to 1300°C soaked for 4 hours and cooled to 1000°C at 5°C/hr. Run No. 80 was treated similarly. Only very small crystals of $LaAlO_3$ were found along with many sharp needles and platelets. These platelet crystals were thought to be borates and samples from run No. 84 made under similar conditions proved to be $LaBO_3$ when checked by X-ray and by wet chemical analysis. Composition was varied from stoichiometric, that is, equimolar La_2O_3+Al_2O_3 (No 87), in an attempt to compensate for the La which was taken out of solution when $LaBO_3$ was crystallized. The ratio of B_2O_3 was also varied widely, from a high of 24.47 m% (No. 84) to a low of 10 54 m% in run No 95. In no case did the $LaAlO_3$ crystals increase appreciably in size over those produced in No. 80 Pure PbO was not tried because in work performed prior to the contract, crystals of $LaAlO_3$ grown in pure PbO averaged 1 mm^3 in size Pure PbO also proved to be extremely corrosive,

TABLE II

MOLTEN SALT RUNS

Run No.	Units	325.84 La_2O_3	101.96 Al_2O_3	195.92 LaF_3	245.19 PbF_2	223.19 PbO	495.96 Bi_2O_3	153.34 BaO	69.62 B_2O_3	Totals	Purpose of Run	Furnace Used (No.)	Crucible Used	Soak Temp (°C)	Soak Time (hrs)	Cooling Rate (°C/hr)	Pour Temp (°C)	Remarks
62	gms moles m %	45.0 0.138 4.43	15.0 0.147 4.72					300.0 1.956 62.75	61.0 0.876 28.10	421.0 3.117 100.00	Solvent selection	4	250 ml	1300	16	2	1000	No pour. No $LaAlO_3$.
63	gms moles m %						300.0 0.605 58.40		30.0 0.431 41.60	330.0 1.036 100.00	Solvent selection	2	250 ml	1300	4	3	600	Timer stuck. Cooled to 600°C Very little glass.
64	gms moles m %							478.4 3.120 77.98	61.3 0.881 22.02	539.7 4.001 100.00	Solvent selection	2	250 ml	1200	4	10	1000	Red and pink brown, bubbly mass.
65	gms moles m %						401.7 0.810 81.00		13.2 0.190 19.00	414.9 1.000 100.00	Solvent selection	Lindberg	250 ml	1000	16	50	700	Glassy melt.
66	gms moles m %							390.0 2.543 61.67	110.0 1.580 38.52	500.0 4.123 99.99	Solvent selection	2	250 ml	1200	16	10	1000	Solid, no pour. No crystals.
67	gms moles m %	113.2 0.347 20.53	35.0 0.343 20.30				401.7 0.810 47.93		13.2 0.190 11.24	563.1 1.690 100.00	Solvent selection	3	250 ml	1340	16	30	1000	Bi_2O_3 and B_2O_3 were premelted together first, then Al_2O_3 and La_2O_3 were added. Many small crystals as cubes and rods.
68	gms moles m %							390.0 2.543 61.67	110.0 1.580 38.32	500.0 4.123 99.99	Solvent selection	2	250 ml	1200	4	5	1000	Good pour. Very little impurity present.
69	gms moles m %	102.0 0.313 19.30	31.5 0.309 19.05				401.7 0.810 49.94		13.2 0.190 11.71	548.4 1.622 100.00	Solvent selection	3	250 ml	1340	16	3 to 1.5	1000	Plug fell on pt can. Spillage.
70	gms moles m %	102.0 0.313 6.60	31.5 0.309 6.51		0.0	0.0	0.0	390.0 2.543 53.59	110.0 1.580 33.29	633.5 4.745 99.99	Solvent selection	2	250 ml	1300	3	3	1030	Small glassy pour. No crystals only many small needles on surface.
71	gms moles m %	91.0 0.279 17.95	28.0 0.275 17.70				401.7 0.810 52.12		13.2 0.190 12.23	533.9 1.554 100.00	Solvent selection	5	250 ml	1340	10	3	900	Leak. Small liquid phase under crust of undissolved material.
72	gms moles m %	100.1 0.307 19.41	28.0 0.275 17.38				401.7 0.810 51.20		13.2 0.190 12.01	543.0 1.582 100.00	Solvent selection	2	250 ml	1340	10	3	400	Leak, stuck Timer. No pour. Very small crystals.
73	gms moles m %	45.5 0.138 10.82	14.0 0.137 10.74				401.7 0.810 63.53		13.2 0.190 14.90	474.4 1.275 99.99	Solvent selection	2	250 ml	1300	10	3	400	Stuck Timer. No pour. Very small crystals just below crust.
74	gms moles m %	102.0 0.313 7.98	31.5 0.309 7.88					312.0 2.035 51.90	88.0 1.264 32.23	533.5 3.921 99.99	Solvent selection	3	250 ml	1300	10	3	1000	No pour, no crystals.
75	gms moles m %	45.5 0.138 10.82	14.0 0.137 10.75				401.7 0.810 63.53		13.2 0.190 14.90	474.1 1.275 100.00	Solvent selection	3	250 ml	1300	[illegible]	3	900	Incomplete solution. Small clear crystals mostly rods growing from underside of crust.
76	gms moles m %	34.2 0.105 7.23	10.5 0.103 7.09				500.0 1.008 69.37		16.5 0.237 16.31	561.2 1.453 100.00	Solvent selection	3	250 ml	1300	3	3	440	Stuck Timer. No pour. Very small crystals.
77	gms moles m %	17.0 0.052 3.85	5.5 0.054 4.00				500.0 1.008 74.61		16.5 0.237 17.54	539.0 1.351 100.00	Solvent selection	2	250 ml	1300	3	5	240	Power shut off when thermocouple opened. No pour. Can leaked. Plug broke. No crystals.
78	gms moles m %	34.2 0.105 7.23	10.5 0.103 7.09				500.0 1.008 69.37		16.5 0.237 16.31	561.2 1.453 100.00	Solvent selection	5	250 ml	1300	4	1	1040	Leak in can but some crystals were larger than usual.
79	gms moles m %	34.2 0.105 5.11	10.5 0.103 5.02				500.0 1.008 49.09		58.3 0.837 40.77	603.0 2.053 99.99	Solvent selection	3	250 ml	1300	[illegible]	5	800	Photo cell burned out. Furnace cooled rapidly to 800°. No crystals of $LaAlO_3$.
80	gms moles m %	69.1 0.212 7.60	21.6 0.212 7.60			400.0 1.792 64.20			40.0 0.575 20.60	530.7 2.791 100.00	Solvent selection	3	250 ml	1300	3	3-5	1100	Sharp needles. No crystals.
81	gms moles m %	69.1 0.212 7.60	21.6 0.212 7.60			400.0 1.792 64.20			40.0 0.575 20.60	530.7 2.791 100.00	Solvent selection	5	250 ml	1300	4	5	1000	Very small crystals but clear.
82	gms moles m %	65.8 0.202 19.20	20.4 0.200 19.01				248.0 0.500 47.53		104.4 0.150 14.26	438.6 1.052 100.00	Solvent selection	3	250 ml	1300	5	5	850	No crystals. Melt is all glass.
83	gms moles m %	69.1 0.212 8.47	21.6 0.212 8.47			400.0 1.792 71.59			20.0 0.287 11.47	510.7 2.503 100.00	Solvent selection	5	250 ml	1300	3	5	880	Small clear cubes.

TABLE II (Continued)

Run No.	Units	325.84 La_2O_3	101.96 Al_2O_3	195.92 LaF_3	245.19 PbF_2	223.19 PbO	495.96 Bi_2O_3	153.34 BaO	69.62 B_2O_3	Totals	Purpose of Run	Furnace Used (No.)	Crucible Used	Soak Temp (°C)	Soak Time (°C)	Cooling Rate (°C/hr)	Pour Temp (°C)	Remarks
84	gms	69.1	21.6			400.0			50.0	540.7	Solvent selection	3	250 ml	1300	4	5	1000	> $LaAlO_3$ only plates.
	moles	0.212	0.212			1.792			0.718	2.934								
	m %	7.23	7.23			61.07			24.47	100.0								
85	gms	69.1	21.6			400.0			40.0	530.7	Solvent selection	5	250 ml	1300	4	1	1040	Very small but clear cubes.
	moles	0.212	0.212			1.792			0.575	2.791								
	m %	7.60	7.60			64.20			20.60	100.00								
86	gms	110.6	17.3			320.0			32.0	479.6	Solvent selection	3	250 ml	1300	4	5	1000	Mostly needles, many small crystals.
	moles	0.339	0.170			1.434			0.460	2.403								
	m %	14.11	7.07			59.57			19.14	99.99								
87	gms	34.6	21.6			400.0			40.0	496.2	Solvent selection	3	250 ml	1300	4	5	900	No $LaAlO_3$ crystals.
	moles	0.106	0.212			1.792			0.575	2.685								
	m %	3.95	7.90			66.74			21.42	100.01								
88	gms		61.2	117.6	345.0				11.4	535.2	Solvent selection	2	250 ml	1300	4	10	1000	No $LaAlO_3$ crystals.
	moles		0.600	0.600	1.407				0.164	2.771								
	m %		21.65	21.65	50.77				5.92	99.99								
88-1	gms	91.0	28.0				401.7		13.2	533.9	Solvent selection	5	250 ml	1340	10	3	1000	Incomplete solution. Cubes of $LaAlO_3$ on bottom of crust.
	moles	0.279	0.275				0.810		0.190	1.554								
	m %	17.95	17.70				52.12		12.23	100.00								
89	gms		61.2	58.0	345.0				11.4	475.6	Solvent selection	2	250 ml	1300	10	10-20	1000	No $LaAlO_3$.
	moles		0.600	0.296	1.407				0.164	2.467								
	m %		24.32	12.00	57.03				6.65	100.00								
90	gms		61.2	10.0	345.0				11.4	427.6	Solvent selection	5	250 ml	1300	4	5	1000	No $LaAlO_3$ only Al_2O_3 plates.
	moles		0.600	0.051	1.407				0.164	2.222								
	m %		27.00	2.30	63.32				7.38	100.00								
91	gms	65.2	40.8		323.6					429.6	Solvent selection	3	250 ml	1400	8	3	1200	Solid, no pour, plates of LaF_3.
	moles	0.200	0.400		1.320					1.920								
	m %	10.42	20.83		68.75					100.00								
92	gms	69.1	21.6			400.0			20.0	510.7	Solvent selection	2	250 ml	1400	8	3	1120	Leak. Very small cubes of $LaAlO_3$.
	moles	0.212	0.212			1.792			0.287	2.503								
	m %	8.47	8.47			71.59			11.47	100.00								
93	gms	45.5	14.0				401.7		13.2	474.4	Solvent selection	5	250 ml	1340	10	3	960	Good pour. Many small $LaAlO_3$ cubes growing from bottom of crust.
	moles	0.140	0.137				0.810		0.190	1.277								
	m %	10.96	10.73				63.43		14.88	100.00								
94	gms	22.7	7.0				401.7		13.2	444.6	Solvent selection	2	250 ml	1340	10	3	800	Leak. No crystals.
	moles	0.070	0.070				0.810		0.190	1.140								
	m %	6.14	6.14				71.05		16.67	99.99								
95	gms	106.7	32.4			400.0			20.0	559.1	Solvent selection	3	250 ml	1300	8	3	1000	Very small but high quality $LaAlO_3$. Incomplete solution.
	moles	0.327	0.318			1.792			0.287	2.724								
	m %	12.00	11.67			65.78			10.54	99.99								
96	gms	54.6	16.8				482.0		15.8	569.2	Solvent selection	5	250 ml	1340	16	3	960	Crucible rotated 16 hours. No crust large crystals 1/2 x 1/2 x 1/4. High quality.
	moles	0.168	0.165				0.972		0.227	1.532								
	m %	10.97	10.77				63.45		14.82	100.01								
97	gms	54.6	16.8				482.00		15.8	569.2	Repeat of # 96	5	250 ml	1340	16	3	920	Small leak and crystals not quite as large as in No. 96 but good quality.
	moles	0.168	0.165				0.972		0.227	1.532								
	m %	10.97	10.77				63.45		14.82	100.01								
98	gms	54.6	16.8				587.8			659.2	Prevent formation of $LaBO_3$	5	250 ml	1340	16	3	950	Can touched muffle wall and tipped over.
	moles	0.168	0.163				1.184			1.517								
	m %	11.07	10.88				78.04			99.99								
99	gms	54.6	16.8				587.8			659.2	Repeat of # 98	5	250 ml	1340	16	3	940	Pedestal top broke and can rubbed against muffle while rotating. Only small $LaAlO_3$ crystals were found.
	moles	0.168	0.165				1.184			1.517								
	m %	11.07	10.88				78.04			99.99								

Molten Salt Crystal Growth (continued)

destroying a platinum crucible usually before the completion of the run. Remeika[1] had similar experiences with pure PbO

2) $BaO-B_2O_3$

No crystals of $LaAlO_3$ were grown in any of the $BaO-B_2O_3$ fluxes In run No. 62, 4 43 m% La_2O_3 and 4 72 m% Al_2O_3 were dissolved in 62.75 m% BaO + 28.10 m% B_2O_3 at 1300°C. The flux was not liquid at 1000°C and there were no crystals in the solid flux. Additional runs were made at higher solute concentrations (13.11 m% in No. 70, 15.86 m% in No. 74) with no success. The flux was not corrosive to platinum.

3) $Bi_2O_3-B_2O_3$

By far the greatest effort was concentrated on this system. The flux was attractive because of its low evaporation and the absence of fluoride. It was however extremely damaging to the platinum crucibles particularly when lead salts had previously been used in the same crucible. Even with new crucibles, lifetime was usually only three or four runs. Failure was usually due to crystallization and cracking of the platinum along grain boundaries.

The phase diagram of the $Bi_2O_3-B_2O_3$ system shows four low melting eutectics exist at about 19, 45, 74 and 76 m% B_2O_3 composition. Bi_2O_3 with 0, 19, 45 and 76 m% B_2O_3 was investigated to determine which composition seemed to give the largest crystals. Run No. 67 used 81 m% Bi_2O_3 and 19 m% B_2O_3. This mixture was premelted and cooled (Run No. 65). Then 20 53 m% La_2O_3 + 20 30 m% Al_2O_3 were added and the entire melt was heated to 1340°C for 16 hours. The result was a mushy melt at the 1000°C pour temperature indicating that complete solution did not occur, but many small well formed cubes and rods were

Molten Salt Crystal Growth (continued)

present. This run was repeated (No. 69) with 10 wt% less solute and without the premelting of the solvent. Unfortunately the plug broke and fell on the can during the soak spilling most of the contents. When this run was repeated as No. 71 and again as No. 72 with a slight further reduction in solute concentration, the platinum crucible leaked and while there was still some indication of incomplete solution the results were inconclusive. The crystals which were salvaged from these runs were of sufficient quality to indicate that if the corrosion problem were reduced and the surface crust which formed could be dissolved, this flux would be suitable for further study.

The 45 m% B_2O_3 composition was tried in run No. 79. 55 m% Bi_2O_3 and 45 m% B_2O_3 were combined with equimolar quantities of La_2O_3 and Al_2O_3. No crystals were observed. In run No. 82 the 76 m% B_2O_3 region was investigated. The flux formed a beautiful glass on cooling but no crystals of $LaAlO_3$ could be found.

It was decided to return to the 19 m% B_2O_3 composition. This time however a number of changes were made. A new crucible which had been used only once before with Bi_2O_3 was used. The soak period was increased to 16 hours and rotated during the entire soak period at 1340°C. The B_2O_3-Bi_2O_3 ratio was 18.93 m% B_2O_3 and 81.07 m% Bi_2O_3 and there was 10.97 and 10.77 m% La_2O_3 and Al_2O_3, respectively, in the total melt. There was no crust when the flux was poured at 960°C. The result was large crystals of $LaAlO_3$ up to 1/2 x 1/2 x 1/4 inches (see Figure 1) together with needles and plates identified as $LaBO_3$. These $LaBO_3$ crystals were easily separated because of their high solubility in the dilute HNO_3 used to remove residual flux from the

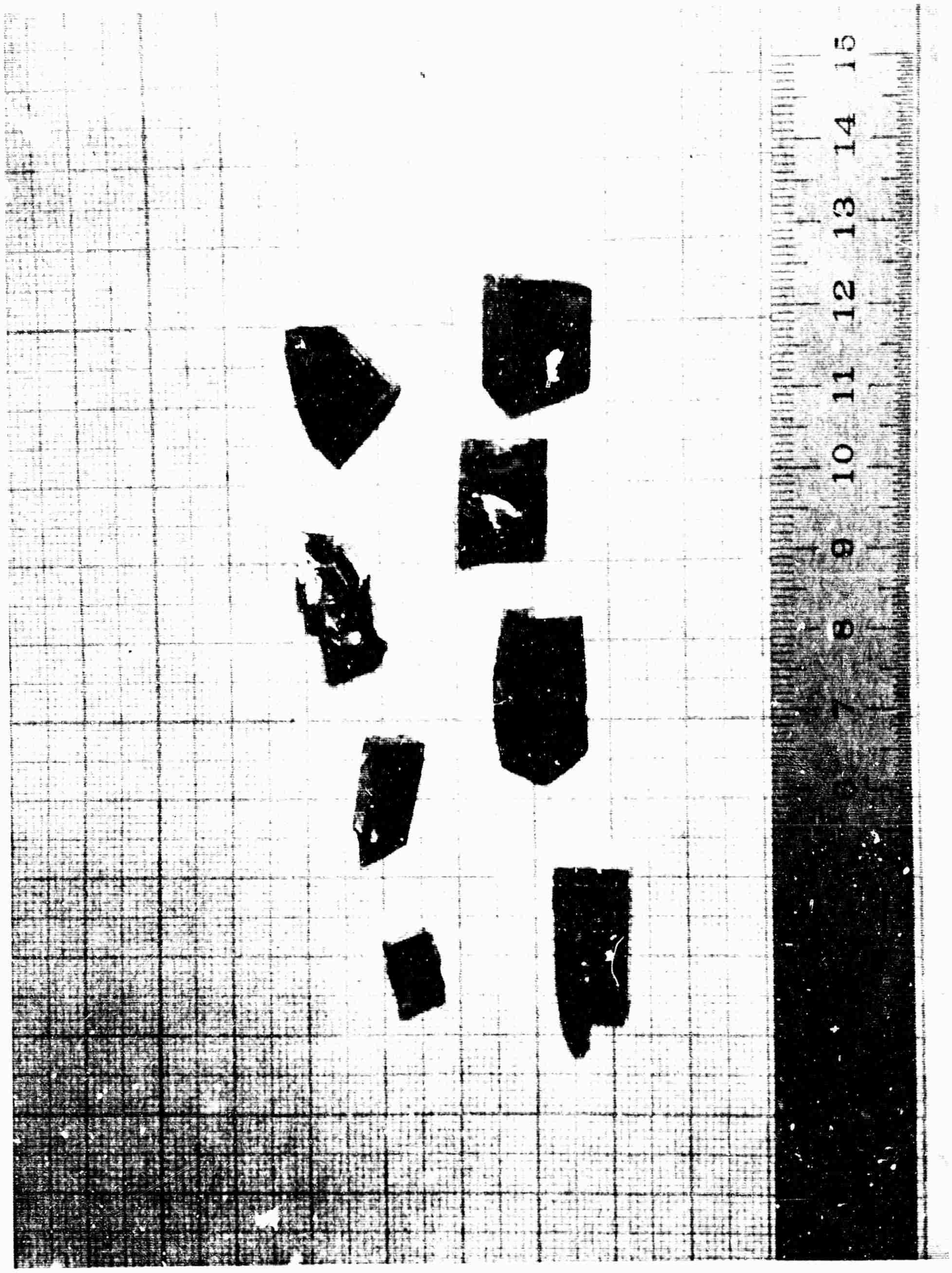

Figure 1

Large Molten Salt Crystals of $LaAlO_3$

Molten Salt Crystal Growth (continued)

$LaAlO_3$. The larger crystals were heavily flux included but the smaller ones were free of inclusions and were of high optical quality (see Figure 2) All were in the form of rectangular parallelepipeds rather than cubes and were a pale yellow color

Run No 99 used Bi_2O_3 with no B_2O_3 added. Crystal size was mostly reduced from No 96 and quality was not improved.

B. Discussion

The crystals produced from the Bi_2O_3-B_2O_3 system are among the best ever grown from a molten salt system in a 250 ml crucible and are far superior to those grown in PbF_2. The crystals grown in PbF_2 melts were only occasionally flux free and of high optical quality. This was because insoluble LaF_3 formed during the soak period and did not dissolve until very high temperatures were achieved. If crystallization of $LaAlO_3$ began before complete solution of LaF_3 occurred or if LaF_3 is precipitated, multiple nucleation, heavily flawed and included $LaAlO_3$ resulted.

Crystals of $LaBO_3$ are found in all runs in which $LaAlO_3$ crystals grow in Bi_2O_3-B_2O_3 fluxes. It is not yet clear at what stage crystals of $LaBO_3$ grow. These crystals, usually found on the surface of the melt as are some $LaAlO_3$ crystals, appear to nucleate after growth of $LaAlO_3$ ends. The $LaAlO_3$ never nucleates on the $LaBO_3$ crystals nor has $LaBO_3$ ever been incorporated into a $LaAlO_3$ crystal the way YAG grows on and around sapphire in melts containing excess Al_2O_3. Solubility studies employing the quenched melt technique will establish when nucleation of the borate begins If the borate growth depends upon exhaustion of Al_2O_3, an excess of this component w l be

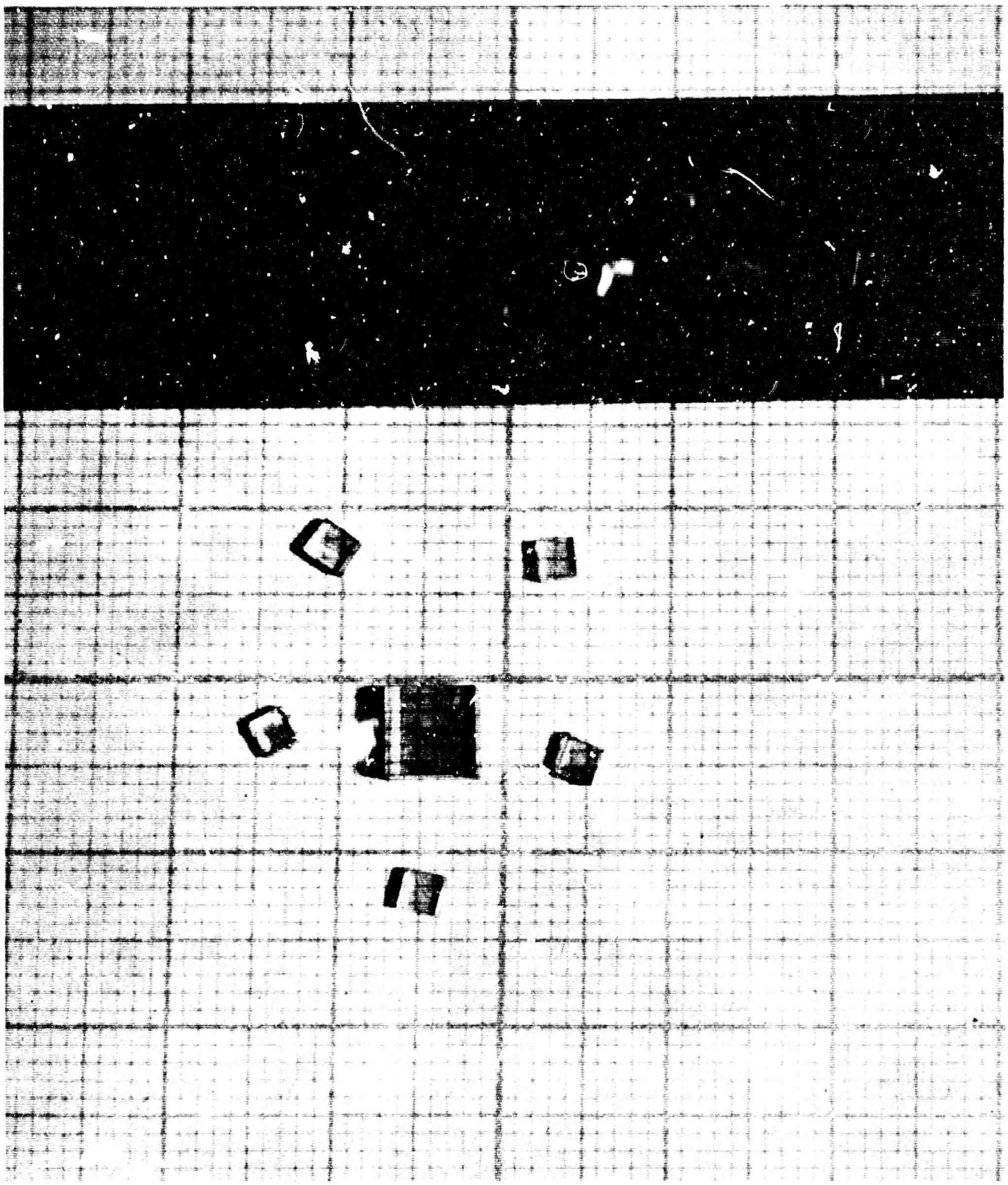

Figure 2

High Optical Quality $LaAlO_3$

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Molten Salt Crystal Growth (continued)

added to increase the $LaAlO_3$ yield.

Optimum growth conditions have not yet been established. While the two runs (98 and 99) using pure Bi_2O_3 with no B_2O_3 were not entirely conclusive and must be repeated it is felt that the 19 m% B_2O_3 composition lies close to an ideal composition The role of B_2O_3 in molten salt fluxes is still obscure, but it seems to increase the rate of solution of oxides and prevent multiple nucleation. The effect is observed in melts used for the growth of YIG and YAG and the effect in solvents PbO, PbF_2 and Bi_2O_3 is similar.

Lead salts attack platinum crucibles mainly in the form of metallic lead reduced from the salt forming an alloy with the platinum. The attack usually has the appearance of small raised beads along the bottom edge of the crucible. This attack can be substantially reduced by the use of an oxygen flow through the furnace during crystal growth. In the case of Bi_2O_3, the attack seems to be in turns of grain growth in the platinum with failure usually due to cracks along grain boundaries. Oxygen flow is relatively ineffective in prolonging platinum life. The combination of Bi_2O_3 with lead salts seems to be particularly fatal with failure occurring in some instances in less than 24 hours. Cans which had previously been used only with Bi_2O_3 usually lasted for three or four runs.

V. HYDROTHERMAL CRYSTAL GROWTH

A. Crystal Growth

During the past report period crystal growth on seeds was achieved in two large autoclave runs (Runs LA-13 and LA-15). In both cases the nutrient was a mixture of ruby and lanthanum oxide. The largest amount of growth obtained was in run LA-15. Weight gains of up to 36% in 9 days were measured on the uppermost seed. The conditions for LA-15 were 480°C growth temperature, 530°C dissolution temperature, 20,000 psi pressure and 8 molal K_2CO_3 as solvent. A photograph of a crystal from LA-15 is shown in Figure 3. Run LA-16 was an attempt to improve on the conditions in run LA-15. The growth temperature was raised 25°C to 505°C and the ΔT increased 5°C to 55°C both of which should increase the yield of $LaAlO_3$. No growth whatsoever occurred nor was any spontaneous nucleation observed. Careful scrutiny of the data did not reveal any factors which could account for the results.

Run LA-17 was a test run under the conditions of LA-15 to evaluate pelletized hydrothermally reacted nutrient. The pellets disintegrated during the run.

Previous observations on mixed oxide nutrient prompted an experiment designed to take advantage of the in-situ reaction of Al_2O_3 and La_2O_3 in the hydrothermal environment. A silver can for run LA-18 was made with two baffles dividing the can into thirds. Ruby was placed in the top section, $LaAlO_3$ seeds in the middle zone and La_2O_3 powder placed in the bottom. The top and bottom temperatures were equalized at 475°C with the middle section about 25°C cooler. Pressure was at 26,000 psi Less than ten percent weight gain resulted, but

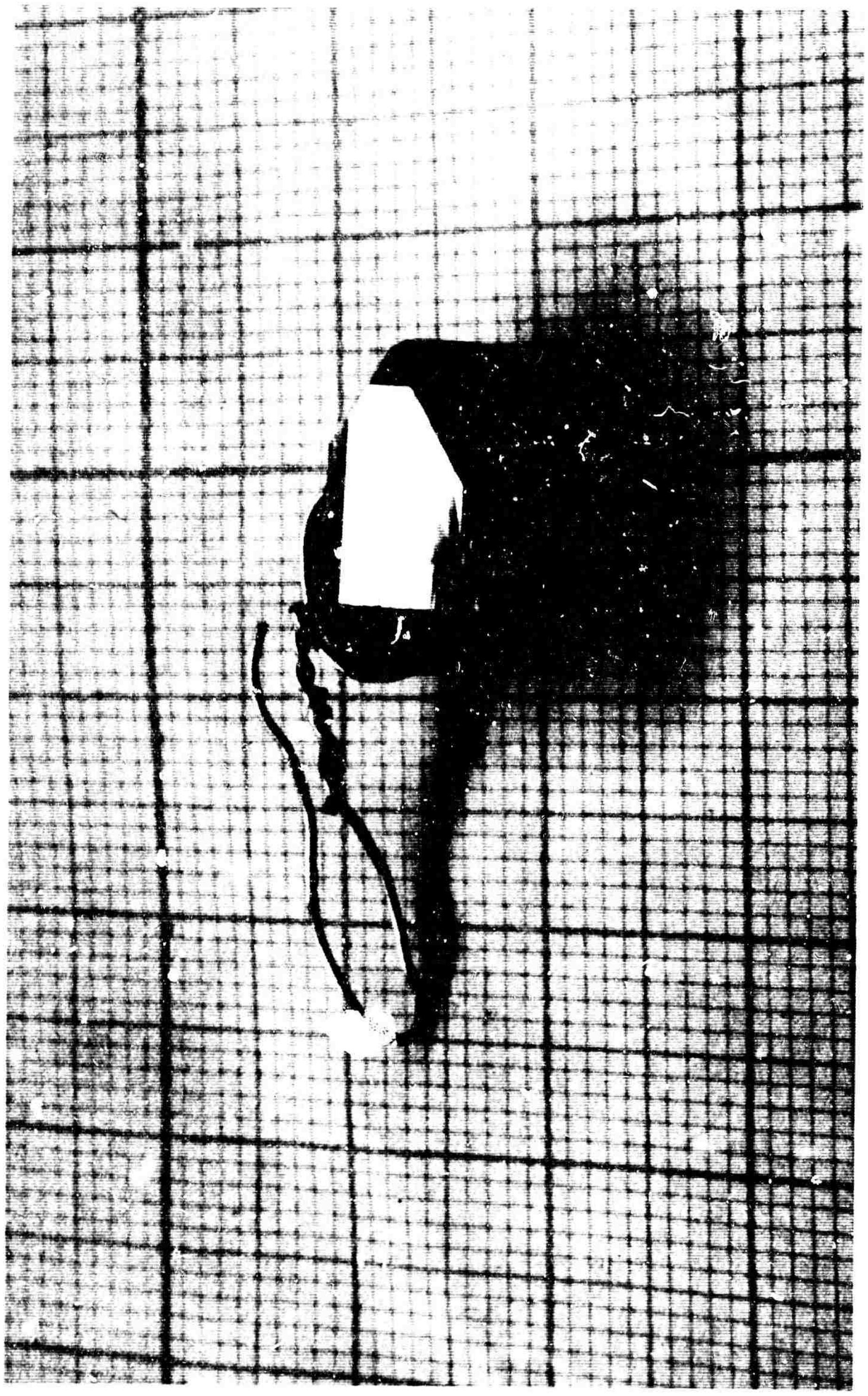

Figure 3

$LaAlO_3$ Hydrothermal Crystal from Run LA-15

all the La_2O_3 in the system had reacted to form $LaAlO_3$ halting further growth A means of reducing the rate of reaction of the La_2O_3 in the bottom of the vessel would greatly increase the yield of $LaAlO_3$ in the seed section.

Run LA-20 was to determine if there was any impurity introduced in the pelletized nutrient. Nutrient for LA-20 consisted of the starting material from which the pellets in LA-18 were fabricated. A tabular summary of the large crystal growth runs attempted during the report period is presented in Table III.

B Nutrient Preparation

The investigation for the preparation of a convenient nutrient form was continued. Two hundred and fifty grams of sintered pills 3/8 inches in diameter by 1/4 inch thick were made. The starting material for the pills was hydrothermally reacted La_2O_3 and scrap flame fusion ruby The granular greenish powder was first boiled in nitric acid to remove any residual carbonates and hydroxides, then dried and sent to National Beryllia Company for sintering. The powder was pelletized and subsequently fired at 3300°F for six hours. Deterioration on continued exposure to the atmosphere has not occurred to the pellets as it had to oxides reacted via sintering only. The difference, we believe, is that in this case the starting material was reacted $LaAlO_3$ rather than the mechanical mixture of La_2O_3 and Al_2O_3 powders. A portion of this nutrient material has been tested to see if it will retain its form on being subjected to the growth conditions. All the pills in run No 17 had completely disintegrated into the coarse powder form the pills were fabricated from.

TABLE III

Run No.	Growth Temperature	Pressure psi	Baffle Area	Molality K_2CO_3 Solution	Duration Days	Nutrient	ΔT	Remarks
LA-7	465°C	17,500	7.5	8	6	$La_2O_3 + Al_2O_3$	60	No growth. Nutrient reacted to form $LaAlO_3$. Heavy S.N. of green color
LA-9	-	--	-	-	-	---		Aborted due to leak
LA-10	400°C	24,000	7.5	7	1	$La_2O_3 + Al_2O_3$	60	Seeds covered with $La(OH)_3$. Short run due to leak.
LA-11	485°C	22,000	7.5	8	2	$La_2O_3 + Al_2O_3$	40	No growth. No S.N.
LA-12	488°C	15,000	7.5	8	6	$La_2O_3 + Al_2O_3$	40	No growth. Some S.N. $LaAlO_3$ of clear color.
LA-13	485°C	22,000	7.5	8	2	$La_2O_3 + Al_2O_3$	50	No S.N. Slight growth.
LA-14	-	--	-	-	-	---		Brand new pressure gauge failed during night causing failure of run.
LA-15	480°C	21,000	7.5	8	9	$La_2O_3 + Al_2O_3$	50	Large amount of growth on seeds.
LA-16	505°C	20,000	7.5	8	11	$La_2O_3 + Al_2O_3$	55	No growth. No S.N.
LA-17	480°C	21,000	7.5	8	12	Pellets of $LaAlO_3$	55	No growth. Pellets disintegrated.
LA-18	475°C	27,000	-	8	3	---	25	Two-zone experiment.
LA-19	-	--	-	-	-	---		Aborted due to seal leak.
LA-20	455°C	25,000	15	8	6	Hydrothermal $LaAlO_3$	50	No growth. No S.N.

S.N. - Spontaneous nucleation of $LaAlO_3$ in growth chamber.

Alumina may serve as a binder if it were added to the hydrothermally reacted $LaAlO_3$ powder before pelletizing and firing. Use of such a binder may require placing a sapphire seed in the growth chamber with the $LaAlO_3$ seeds to act as a sink for excess binder

C. Autoclaves

Early in the report period one of the vessels developed a leak during a run. After cool-down when the vessel could be opened the external portion of the fill was found to be basic. A meticulous examination of the silver can revealed a porous section of weld at the top of the can. Potassium carbonate solution had leaked through the porous section of the weld causing very small longitudinal stress corrosion cracks to appear in the seal area. Grinding the seal surface until no evidence of cracks was found by dye penetrant check and then making a test run was tried repeatedly. The vessel leaked every time through the same cracks. The first time the cracks were found they were located by scribing marks on the autoclave body In this way we could tell that they were the same cracks and not new cracks appearing each time. We also found that the cracks transcended the entire seal region. A photograph of one of the cracks in the seal area is shown in Figure 4. The photograph is of a reflection in a dental mirror With the cracks in the seal area the vessel is useless. We therefore attempted to repair the vessel The autoclave was bored out to match the inside diameter of the threaded section above the seal area A liner was fabricated from a 316 stainless steel seamless drawn tube by welding a plug in the bottom. The liner was shrink-fitted into the autoclave after which the seal surface was machined.

Airtron, a division of Litton Industries

Figure 4

Cracks in the Seal Area of an Autoclave

Hydrothermal Crystal Growth (continued)

A drawing showing the liner in place in the autoclave is shown in Figure 5. Successful testing of the repaired vessel to 500°C and 25,000 psi simultaneously has been completed. Routine use of the vessel will begin at once.

Steps have been taken to prevent the recurience of seal attack just described, i.e., failure due to caustic leakage through a porous section in the weld of a silver can. All welds are dye penetrant checked prior to use to locate any porous areas in the weld.

D. Discussion

The crystal growth and spontaneous nucleation observed to date may be the result of a non-equilibrium condition arising out of the use of a two-component nutrient Lanthana and alumina have higher solubilities than lanthanum aluminate does under the same conditions. As the hydrothermal conditions were imposed on the oxide mixture the Al_2O_3 probably dissolved first and left a surplus of La_2O_3 over stoichiometry in the nutrient section of the vessel. The excess La_2O_3 could then dissolve at a later time or a higher temperature, migrate to the growth zone through the baffle and there react with the Al_2O_3 and cause supersaturation of the solvent with respect to lanthanum aluminate. Crystal growth would begin as a result of the supersaturation and would continue until the Al_2O_3 had all reacted with the La_2O_3.

This hypothesis gains strong support from a number of consistent data. Crystal growth and spontaneous nucleation has occurred only when the nutrient is made up of the mixed oxides. Complete reaction of the mixed oxides to form lanthanum aluminate occurs in every

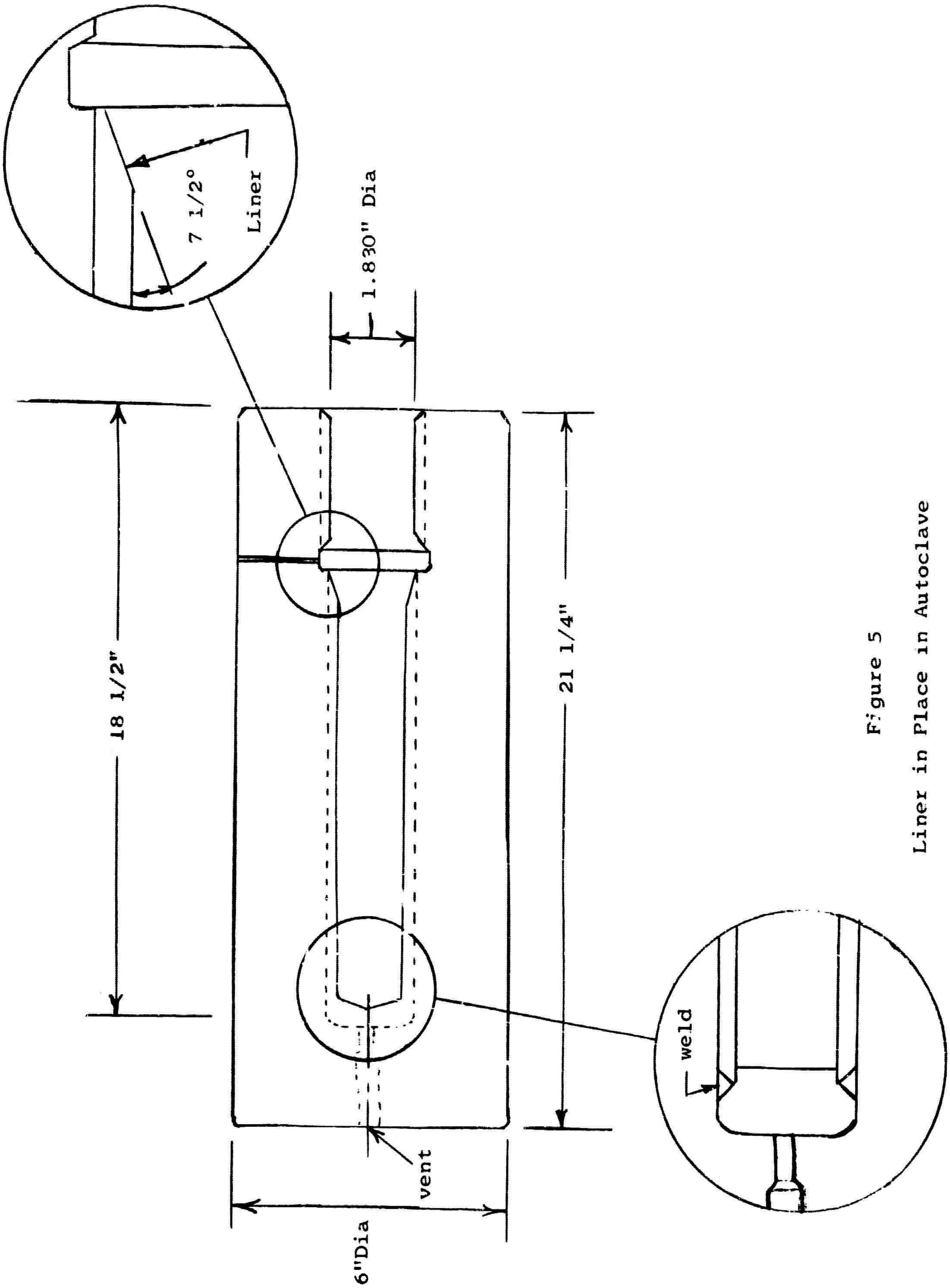

Figure 5

Liner in Place in Autoclave

Hydrothermal Crystal Growth (continued)

run, even in aborted runs of less than 24-hour duration. All attempts to grow lanthanum aluminate in the large autoclaves using $LaAlO_3$ as nutrient have failed to produce any recrystallization. Note particularly runs LA-15 and LA-17 where operating conditions are identical except for a 5°C difference in ΔT. A large amount of growth was obtained in LA-15 using a mixed oxide nutrient while in run LA-17 a lanthanum aluminate nutrient yielded no growth at all.

However, growth on seeds using the $LaAlO_3$ for nutrient has been obtained in the Tem-Pres apparatus using 1/4 inch diameter capsules. Solvent concentration was 7 molal, pressure was 20,000 psi, growth temperature was 475 to 500°C. The main stumbling block to accomplishing equivalent results in the large system is the translation of temperature conditions from the Tem-Pres to the large autoclaves. The most obvious, and at the same time the most difficult solution would be internal temperature measurements of the operating system. However, due to the technical difficulties, a relationship between external temperatures is the most expedient method.

VI. OPTICAL MEASUREMENTS

Absorption spectra from 6500-10,000A° of an undoped flux grown plate of $LaAlO_3$ (amber in color) as well as of hydrothermally grown (green) and flux grown (red) crystallites of $LaAlO_3$:Cr have been studied by passing light from a tungsten filament lamp through the sample and suitable combinations of Corning and Wratten filters to a 0.5 meter Jarrel-Ash spectrometer. The light was detected by using either S-1 or S-5 photodetecting surfaces. The filters were chosen to eliminate undesired orders in the spectrometer. Relative spectral transmissions were obtained by comparing the detected signal with a crystal in front of the spectrometer slit to that with the crystal removed.

Fluorescent lines of the doped samples were excited by means of a tungsten filament lamp focused on the crystallites, in a glass vial, through suitable filters. The emitted light passed through filters before entering the slit of the spectrometer, in order to eliminate undesired orders. Detection was by means of an S-1 photomultiplier.

When the undoped plate was illuminated by ultraviolet light it was observed to fluoresce orange-red to the eye. The flux grown $LaAlO_3$:Cr emitted a strong line at 7356A° that was about 10A° wide. All other emissions were much weaker. These included an emission band, between 7600A° and 7356A°, whose strongest components occurred at 7495A° and 7430A°. Lines also occurred at 7720A°, 7785A°, 7230A° and 7280A°. The hydrothermal sample was very similar in its fluorescence in that it also emitted its strongest line at 7356A° and had a much weaker emission band between 7600A° and this line. The band's strongest components were at 7495A° and 7430A°. Lines were also observed at 7720A°,

Optical Measurements (Continued)

7820A°, 7230A° and 7275A°.

The strong line at 7356A° is due to Cr^{3+} emission. We assume that the weak lines and bands around it are due to phonon assisted transitions.

Typical transmission curves are shown in Fig 6. The ordinate scale is logarithmic. Resolution is about 200A°. Any one curve gives the relative transmission of one sample and is unrelated to the curves of the other samples.

The transmission measurements on the doped samples were made on small crystals whose sides were neither plane nor parallel. The crystals were moved and rotated between measurements in the two wavelength regions, longer and shorter than 6000A°. Accordingly, the thickness of the crystal through which the transmission was measured was different in the two spectral regions. Although the relative transmissions are made equal at 6100A°, 5300A° and 6000A° on the curves of the flux grown doped and undoped, and hydrothermally grown crystallites respectively, the absolute magnitudes of the slopes of the curves in the two regions are independent because the slope of a transmission curve will depend on the thickness of the sample. Due to the small size and irregular shape of the crystals the results obtained are qualitative.

The hydrothermal crystallites had two absorption maxima centered at 5900A° and at 4600A°, with a transmission maximum centered at 5300A°. The flux grown sample appeared to have an absorption maximum at 4200A°. The absorption of both doped crystal samples decreased toward long wavelengths until 6600A°. At this point the absorption of the hydro-

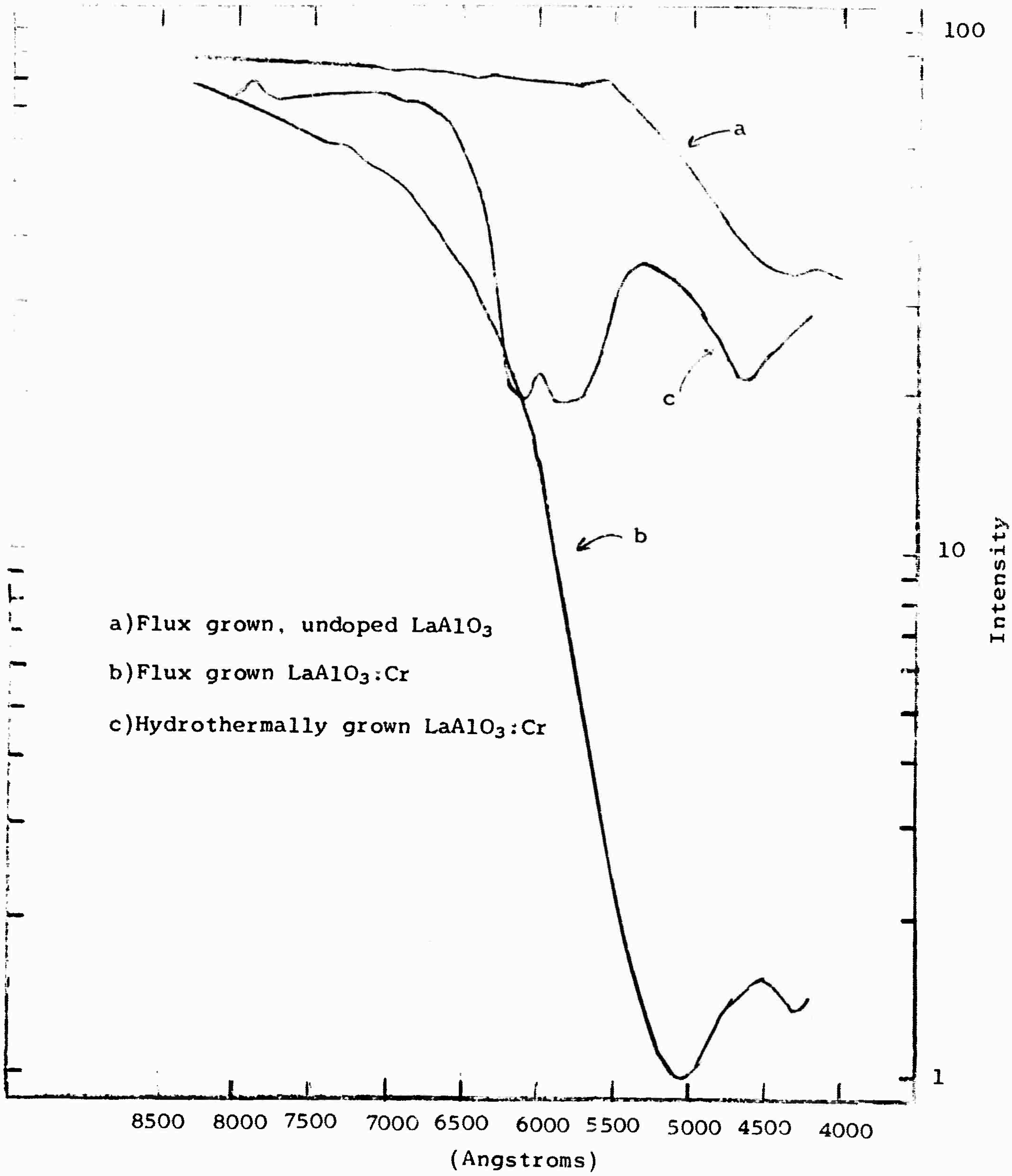

Figure 6

Transmission vs. Wavelength of $LaAlO_3$ and $LaAlO_3$:Cr

Optical Measurements (continued)

thermal sample leveled off to a low absorption region for longer wavelengths. The absorption of the flux grown sample did not appear to level off, but continued to decrease at longer wavelengths. The absorption of the undoped plate increased from 5600A° to 4500A° and then appeared to roughly level off to a region of high absorption below 4500A°. At wavelengths longer than 5600A°, the undoped sample showed low absorption.

It can be seen that the absorption curve of the hydrothermally grown crystallites would be similar to that presented by Forrat, et al[2] for 0.5% Cr doped $LaAlO_3$. The curve of the flux grown $LaAlO_3$:Cr crystallites is similar to that of Forrat's undoped crystal, colored red, containing what he felt were V centers due to randomly distributed vacant La^{3+} sites. He was able to remove the red color by heating in a hydrogen or CO atmosphere. It would be of interest to see whether our flux grown doped sample becomes green after such treatment. The occurrence of the fluorescence line at 7356A° indicates the presence of Cr^{3+} in both the flux and hydrothermally grown samples, Possibly the presence of V centers causes sufficient absorption to mask that of the Cr^{3+} in the flux grown sample. Our undoped plate had an absorption curve similar to Forrat's undoped crystals after he heated them in the hydrogen or CO atmosphere. These results on our flux grown samples might be expected since the doped sample was grown in PbF_2, possibly leading to La^{3+} vacancies, while the undoped sample was grown in Bi_2O_3-B_2O_3.

VII. SUMMARY AND CONCLUSIONS

The following conclusions can be drawn from the work of this period:

1) $LaAlO_3$ crystals can be grown from molten PbF_2, PbO, PbO-B_2O_3, Bi_2O_3 and Bi_2O_3-B_2O_3.

2) Growth in Bi_2O_3-B_2O_3 melts produces the largest and best quality crystals of the solvent systems investigated.

3) Platinum crucible failure is not a major problem when crucibles are used with only Bi_2O_3.

4) Crystal growth and spontaneous nucleation in the large hydrothermal system may be due to a non-equilibrium situation resulting from the use of the mixed oxides as nutrient.

5) Chromium fluorescence has been detected from both flux grown and hydrothermally grown $LaAlO_3$:Cr.

6) The hydrothermally grown $LaAlO_3$:Cr has a transmission maximum at 5300A° which was not observed in the absorption spectrum of the flux grown $LaAlO_3$:Cr. The shape of the latter absorption spectrum may be due to La^{3+} vacancies.

VIII. PROGRAM FOR NEXT PERIOD

1. Optimize Bi_2O_3-B_2O_3 ratio.

2. Use both the quenched melt and sealed tube techniques to determine solubility and phase equilibria of $LaAlO_3$ in Bi_2O_3-B_2O_3 melts.

3. Growth $LaAlO_3$ crystals from Bi_2O_3-B_3O_3 doped with varying amounts of chromium.

4. Determine the absorption and fluorescence spectra of doped and undoped $LaAlO_3$.

5. Optimize growth conditions for $LaAlO_3$ in Bi_2O_3 using 250 ml crucibles and 5-1/4" can.

6. Determine effect of variables such as temperature pressure, % fill, ΔT and seed orientation on hydrothermal crystal growth and crystal quality.

7. Grow large crystals of $LaAlO_3$ doped and undoped from hydrothermal systems.

IX. REFERENCES

1. J.P. Remeika, J.Am.Chem.Soc. 78, 4259 (1956).

2. F.Forrat, R. Jansen, and P. Trévoux, Comp.Rend. 256, 1271 (1963).